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(54) Title: OLEFIN POLYMERISATION PROCESS

(57) Abstract

The invention relates to the use of a partially hydrolysed aluminum alkyl material in oligomeric form as a scavenger in an olefin polymerisation process, said material containing less than 20 % by Al of unreacted aluminum alkyl, preferably less than 15 %, especially less than 10 %.

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Olefin Polymerisation Process

Field of invention

The invention relates to olefin polymerisation processes, particularly those using bulky ancillary ligand transition metal catalysts components and especially solution, slurry or high pressure polymerisation processes for making ethylene homo- and co-polymers.

The term "bulky ancillary ligand transition metal catalyst component" refers to compounds having hydrocarbyl or hetero-atom containing groups bonded to the transition metal. The phrase "bulky ancillary ligand" refers to ligands which have a stable bond with the metal and are generally inert to the polymerisation reaction mechanism. The ligand groups may include cyclopentadienyl groups which are mono or polynuclear or amido groups. The components include metallocenes. The cyclopentadienyl groups may have one or more carbon atoms replaced by other atoms such as hetero atoms e.g. phosphorus.

The term "metallocene" is used herein to indicate compounds having π-bonds linking a moiety to a transition metal. As will be explained the moiety may include a five-membered ring of a cyclopentadienyl type. One or two such π-bonds may be present in the compound.

The term "copolymer" is used herein to indicate polymers derived of two or more copolymerisable monomers and so includes terpolymers etc.

The term "olefin" is used herein generically to include all components containing a double bond active for addition polymerisation including linear and cyclic olefins such as styrene , vinyl compounds and poly-enes.

Background of the invention

EP 277 003 (Exxon) and 277 004 disclose the use of bulky anions as cocatalysts with metallocene cations in olefin solution polymerisation and in high pressure polymerisation (cf. Example 32 of EP 277 003).
EP 427 697 (Fina) proposes use of an aluminum alkyl ;
US 5 153 157 (Exxon) similarly uses an organometallic compound.
EP 436 399 (Idemitsu Kosan) uses hybrid catalysts in order to produce broad molecular weight distributions.

EP 481 480 (Idemitsu Kosan) proposes use of a small amount of an organo aluminum compound with a metallocene catalyst system in making propylene based oligomers.
EP 485 820 and EP 485 822 (Hoechst) disclose mixed catalyst systems for the preparation of polypropylene which employ both alumoxane and bulky anions.
EP 504 418 (Idemitsu Kosan) discloses in Example 45 the combined use of bulky anion and alumoxane cocatalysts in the preparation of ethylene norbornene copolymers in solution at low temperatures and low pressures.
EP 505 973 (Idemitsu Kosan) uses related catalyst systems for styrene polymerisation.
EP 513 380 (Idemitsu Kosan) uses related catalyst systems for syndiotactic polymerisation.

Use of organo-aluminum compounds as co-catalysts is well known in connection with classical heterogeneous $TiCl_3$ based olefin polymerisation catalysis.

Use of organo-aluminum compounds as scavengers to remove catalyst poisons is also known. In EP 206 794 (Exxon), concerning gas phase polymerisation, triethyl aluminum was used as a scavenger in Example 7; whilst in Example 4

discusses the use of methyl alumoxane injected in Example 1 for a scavenging function.

EP 423 100 (Fina) mentions bulky non-coordinating anions and alumoxanes, see column 10. In that passage it is stated that "alumoxane ... need not, and preferably is not, used in carrying out the present invention where ..." etc. The reference to "alumoxane" is to alumoxane as a cocatalyst. Continuous processes are not disclosed. Column 11 goes on to say : "Alumoxanes usually are not employed in the present invention with cationic metallocenes and if they are used they are used in amounts well below the aforementioned range preferably providing an Al/Me ratio of no more than 10 and preferably no more than 1." EP 423 100 includes no examples.

WO 93/14132 (Dow) discloses a polymerisation process for monocyclopentadienyl compounds and bulky anions using alumoxanes as scavengers. Page 4 indicates use of C_1 to C_4 alkylalumoxanes but there is no specific disclosure of tertiary carbon containing alkyl groups; nor is there an indication of the amount of unreacted aluminum alkyl. Methylalumoxane is preferred; commercially practised preparation methods therefore contain significant levels of unreacted trimethylaluminum which can only be removed by special measures not described in WO 93/14132.

In polymerising olefins in continuous systems the build up of highly volatile polar material can cause serious operations problems. This poisoning is believed to be assisted by catalyst which has become removed from the reaction zone. In extreme cases poisoning can necessitate shutdown of the reactor ; in minor cases it can impede the efficiency of the process and limit the

safe rate at which polymer is produced. In such continuous systems furthermore, extraneous polar materials particularly those of Lewis base type may build up and exercise a negative influence on the apparent efficiency of the process, most commonly as evidenced by the catalyst activity. These effects overall can be particularly problematical with catalyst systems where a lot of polymer is produced for a given amount of catalyst such as polymerisation processes at elevated temperature and pressures (under which conditions bulky ligand catalysts can be highly active) or processes employing bulky anions as cocatalysts or activator in a ratio to the transition metal compound which is very low.

Particularly with processes involving recycle systems, the build up of volatile poison materials may influence the process efficiency and stability.

It is amongst the objects of the invention to provide a continuous process using a catalyst system combination which permits efficient use of the catalyst system components; reliable polymerisation performance over prolonged continuous processes; and yields of polymers of desired higher molecular weight and/or with low metal content.

<u>Summary of the invention</u>

According to the first aspect of the invention there is provided use of a partially hydrolysed aluminum alkyl material oligomer as a scavenger in an olefin polymerisation process, said material containing less than 20 % by Al on the basis of total Al-content of unreacted aluminum alkyl, preferably less than 15 %, especially less than 10 %. Use as a scavenger can be

recognised by the effect of the oligomer introduction and by the manner of its introduction to the olefin polymerisation process. Possible ways of determining the percentage of unreacted aluminum alkyl are indicated in the Examples.

Preferably the aluminum alkyl contains an alkyl group with at least two carbon atoms and has substantially no co-catalytic activity, preferably having an alkyl group containing a tertiary carbon atom. Such oligomers can be prepared in one-step hydrolysis processes to give low levels of unreacted aluminum alkyls, yet form effective scavengers. Generally their cocatalytic activity is low under prevailing process conditions.

Suitably the material is used in conjunction with an olefin catalyst system comprising a bulky ancillary ligand transition metal component and a bulky anion component. Conveniently the material is used in a process involving a recycle of non-reacted polymerisation diluents including monomers and/or inert materials. Suitably the material is used as a scavenger by adding it to a catalyst system (prior to the introduction of the catalyst system to a polymerisation reactor) and/or separately to a polymerisation reactor feed before or after the introduction of the feed to the reactor.

Preferably the material is used in a polymerisation process performed at a pressure of at least 100 bar preferably at from 500 bar to 3000 bar. Under such conditions generally at temperatures in excess of 150°C, the invention can permit effective scavenging over a prolonged period of continuous reaction as few volatiles build up which disrupt or reduce the efficiency of polymerisation.

In a second aspect of the invention, there is provided a continuous process for olefin polymerisation including injecting as catalyst a reaction product of a bulky ancillary ligand transition metal component and a bulky anion precursor into a reactor, feeding monomer to the reactor and withdrawing polymer therefrom in which there is additionally added as a scavenger an oligomer of a partially hydrolysed aluminum alkyl oligomer containing less than 20 % by Al of unreacted aluminum alkyl, preferably less than 10 %.

In a third aspect of the invention ther is provided a continuous process for olefin polymerisation including injecting as catalyst a bulky ancillary ligand transition metal component and a bulky anion precursor or a reaction product thereof into a reactor, feeding monomer to the reactor-polymerising monomer at from 100 to 300°C at up to 3000 bar in the reactor and withdrawing polymer from reactor in which there is additionally added as a scavenger an oligomer of a partially hydrolysed aluminum alkyl oligomer.

The scavenger should be introduced in such a way that it has sufficient opportunity to react with impurities in the monomer feed , in any solvent used or in the catalyst supplied . The scavenger may be fed in more than one place to deal with any residual killer for example in a high pressure recycle stream or impurities created by the catalyst formation reaction. The scavenger should preferably not be combined with the catalyst until the bulky ligand transition metal component and the bulky anion precursor have had opportunity to react. The scavenger may be introduced to a reactor into which the catalyst components are added separately for catalyst formation <u>in situ</u> during polymerisation.

It is believed that, in use, these high molecular weight hydrolysed components react with any impurities. In this way products are formed which precipitate out with the polymer in the separation process and which do not remain volatile , even at high pressure and/or temperatures, and

do not remain in the reaction system and can be seperated therefrom.

The alumoxane may be derived from a wide variety of aluminum alkyls. Suitably the mol ratio of the transition metal component and the cocatalyst is from 1:10 to 10:1, preferably from 1:1 to 3:1. Advantageously the mol ratio of aluminum in the scavenger to the transition metal in the transition metal component is from 1:1 to 500:1, preferably from 2:1 to 50:1.

Preferably the partially hydrolysed aluminum alkyl contains less than 20 % by Al of unreacted aluminum alkyl, preferably less than 10 %. The presence of unreacted aluminum alkyls may be disadvantageous in that there is a risk that they accumulate in the reactor system because of their volatility and hence start to interact with the polymerisation reaction, particularly with transition metal components which are chemically less stable . The amount of unreacted aluminum alkyl can be reduced and the molecular weight increased if required by performing additional hydrolysis , preferably by the slow addition of water under carefully controlled conditions . This can be useful particularly with lower alkyl derived oligomers.

Suitably the aluminum alkyl precursor has an alkyl group with from 2 to 20 carbon atoms. Generally the aluminum alkyl precursor may be of the general formula AlR_3 wherein each R may be the same or different, at least one R is a hydrocarbyl group such as an alkyl, aryl, arylalkyl, alkylaryl or alicyclic (cyclo-aliphatic) group. Optionally other R's may be a halogen such as chloride or be alkoxy, anyloxy, arylalkyloxy, alkylanyloxy or alicyclic oxy groups.

Preferably the hydrocarbyl group is a C_2 to C_{20} group, especially a group with a tertiary carbon atom such as

iso-butyl which imparts good solubility in organic solvents to the resultant alumoxane. It is to be noted that methyl alumoxane is preferably not used. Its use might lead to a broadening of the molecular weight distribution if it enters into the polymerisation reaction because it may perform a cocatalyst role. Using oligomers derived from aluminum alkyl precursors with alkyl groups having more than 2 carbon atoms (or derived to an extent of at least 90% from such aluminum alkyl precursors), hydrolysis may be continued until all or almost all aluminum alkyls have hydrolysed without undue overhydrolysis and formation of $Al(OH)_3$. Such oligomers have a relatively high molecular weight and the alumoxane contains only a low portion of volatile, unreacted starting materials. The alumoxane species generally identified as the most effective cocatalyst, methylalumoxane, is not the preferred component in the invention. Higher alumoxanes derived from AlR_3 where R_2 > 2 or 3 may permit higher polymerisation temperatures and are less volatile and less prone to yield breakdown products which remain in the reactor system.

Advantageously the alumoxane has a molecular weight in excess of 800, preferably in excess of 1600, especially 2000. It may also have sufficient hydrocarbyl functionality to be easily removed with the polymer. In this way the alumoxane residue (or its reaction product with poisons) does not accumulate in a continuous polymerisation process and is removed as part of the polymer from the system, permitting stable polymerisation in prolonged continuous runs (e.g. more than 24 hours).

The bulky anion and alumoxane act highly synergistically in terms of the productivity based on total metal. Alumoxane other than methylalumoxane are fairly inefficient cocatalysts ; the bulky anion is in theory highly efficient but it is poison sensitive .

In practice even with the systems described in EP 277 003 and 277 004 productivities can be fairly modest. The invention permits the use as catalysts of low levels of metallocene and bulky anions in turn reducing the associated amount of scavenging compounds needed. With suitable combinations industrially available monomer feed streams can be used on a commercially scale. In view of the synergism and high productivity, there is a surmised possibility that the alumoxane does not act merely as scavenger but interacts as a modifier with the metallocene or bulky anion in a manner different from the usual cocatalytic role so as to enhance the performance of the polymerisation catalyst systems.
The bulky ancillary ligand transition metal component is preferably a neutral four cordinate compound, reactable in the presence of the cocatalyst to the + 1 state. The transition metal may be a Group 3 to 10 transition metal such as titanium, zirconium, hafnium, vanadium, tungsten etc. The preferred structure is [L] [L'] M (X) (X) where L and L' are the bulky ligands and X is a monovalent leaving group. The ligands and leaving groups may be bridged between the ligands and/or between the leaving groups or the ligand and leaving group may be bridged. The total number of bulky ligands and leaving groups may vary from one upwards, consistent with the metal oxidation state. Preferably the bulky ligand is a cyclopentadienyl group so that the component is a metallocene.

The metallocene may have the general formula (1) $(LS)ZX_1X_2$ wherein Z is a Group 3 to a Group 10 transition metal preferably zirconium, hafnium or titanium; X_1 is a leaving group which may be an anionic ligand reactable with a non-coordinating anion; X_2 is hydride or a hydrocarbyl or hetero radical; and (LS) is a ligand system comprised of one or more, suitably 2 and possibly 3, ancillary ligands sufficient to complete the coordination number of Z. Whilst (X) is described as a leaving group, it may be reacted and transformed into a group which is separated from the neutral compound when a cation in the +1 state is formed. Only one of the groups may leave; a remaining X groups may be part of the cation formed.

The bulky anion precursor may be any one of those described in the patent literature in EP 277004 and 277003 (Exxon), in EP 418044, EP 495375 (Dow) and in EP 426637 (Fina). The precursor may be formed into an anion by any of the methods described in the art ranging from ion exchange methods using ammonium salts and proton donation or silver salt reaction right up to abstraction of a group from the transition metal component to form the anion. The precursor for the cation may be formed by an alkylation step which may be performed <u>in situ</u> in the polymerisation reactor, e.g. by using a suitable aluminum alkyl provided it does not significantly poison the catalyst under the prevailing conditions.

The term "bulky anion precursor" refers to a compound which by a suitable ion exchange, redox or abstraction reaction form a "bulky anion" which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge bearing metal or metalloid atom.

The bulky anion should be stable relative to the cation under ambient conditions before infection, that is to say not react for example by transfer of a fragment thereof, so as to form a neutral reaction product. The bulky anion should not coordinate to the cation formed by the metallocene so as to block olefin monomer access and should be sufficiently labile to permit olefin insertion in polymerisation conditions. The bulky anion may be represented by the following general formula: $[(M')^{m+}Q_1Q_2...Q_n]^-$ wherein M' is a metal or metalloid selected from the Groups subtended by Groups V-B to V-A of the Periodic Table of the Elements, i.e. Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A and V-A; Q_1 to Q_n are selected, independently, from the Group consisting of hydride radicals, dialkylamido radicals, alkoxide and aryloxide radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and any one, but not more than one, of Q_1 to Q_n may be a halide radical - the remaining Q_1 to Q_n being, independently, selected from the foregoing radicals;

m is an integer from 1 to 7;

n is an integer from 2 to 8; and

n - m = d (d being preferably 1).

Bulky anions which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula: $[BAr_1Ar_2X_3X_4]^-$;

Wherein:

B is Group III-A metal, preferably boron, in a valence state of 3;

Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals preferably containing from 6 to 20 carbon atoms and may be linked to each other through a stable bridging group;
and X_3 and X_4 are radicals selected, independently, from the group consisting of hydride radicals and halide radicals, hydrocarbyl radicals containing preferably from 1 to 20 carbon atoms, substituted-hydrocarbyl radicals preferably wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to 20 carbon atoms, hydrocarbyl-substituted metal (organo-metalloid) radicals wherein preferably each hydrocarbyl substitution contains from 1 to 20 carbon atoms said metal is preferably selected from Group IV-A of the Periodic Table of the Elements and the like.

In general the bulky anion precursor contains at least one, generally two or three substituted phenyl groups bonded to a boron atom or a multi boron compound in which the boron or other metalloid atom is shielded by bulky group and not reactive with the transition metal component.

The polymerisation processes to which the invention applies are continuous. Continuous processes need to be stable so that polymer of particular properties can be obtained. Often using monomer streams or other materials introduced contain potential poisoning impurities. Whilst metallocene based catalyst systems permit high activities they tend to be prone to reduction of the activities resulting from poisons.

Suitably the catalyst is unsupported and preferably the polymer and monomer are in a homogeneous medium. Advantageously the reaction temperature is from 100 to 300°C preferably from 150 to 280°C. In these homogeneous

conditions the scavenger compound of the invention may be particularly useful in improving the process. The invention is especially applicable to a high pressure process at a pressure of from 50 (fifty) to 3000 bar , preferably from 500 to 2500 bar , where the conversion on each pass is limited and there is a high need to avoid accumulation of poisons and scavengers in order to obtain stable process conditions.

The process may be high pressure polymerisation in a homogeneous single phase or in two-phases, with or without unreactive diluents at pressures and temperatures generally above the polymer melting point. If appropriate the catalyst system may be added in a dissolved, homogeneous state. Such processes may be performed adiabatically.

By the assistance of the effective scavenging it may be possible to operate at temperatures above those otherwise possible, achieving still higher yields and / or single pass conversions in polymerisation systems which use adiabatic polymerisation reaction conditions.

The process may also be a solution process with catalyst dissolved or a slurry process with the catalyst on a support suspended in a polymerisation reaction diluent.

The high pressure process may include a catalyst killing step particularly if significant amounts of active catalyst remain after polymerisation. The killer may be a monodisperse non-volatile polar oligomer (MW > 3000) which is not easily extracted in any recycle step following separation. Killers with high O/C ratios and preferably high OH/C ratios are preferred. Polypropylene glycol (MW = 2200, MWD = 1.3) may be used. The killer may also be a volatile component which is thermally stable at separating and recycling conditions. The volatile killer may be water but could be another

compound having a low molecular weight, having a reactive O,N or S moiety such as CO_2, CO, NH_3, SO_2, SO_3, N_2O alohols, diols, triols, ethers, aldehydes, ketones carboxylic acid and diacids, their anhydrides or esters, amines, amides or imides or hydrogen peroxide or alkyl hydroperoxide or a non-volatile component which decomposes to the above volatile compounds. Less than a stoichiometric amount of killer (killer/TM mole ratio around 0.1) may be used. The alumoxane scavenger present according to the invention interacts in catalyst killing. Killer added, either volatile (i.e. water) or non-volatile (i.e. PPG), may react preferentially with the alumoxane. The alumoxane may be itself deactivated (see WO 92/14766).

Suitably the process is performed overall in such a way as to provide a productivity in g PE per gram of bulky non-coordinating anion of at least 50.000, preferably at least 100.000, especially at least 150.000.
The invention is illustrated by the Examples.
TM refers to the transition metal component which is a precursor of the metallocene cation ; activator refers to the precursor or the bulky, non-coordinating anion which is cocatalytically active and is referred to by the abbreviation CC.

The high pressure experiments were performed in adiabatic, stirred, autoclave reactor having a catalyst mixing vessel connected by a metering pump to the top of the autoclave, a separating system including a high pressure separator for separating unreacted materials

from polymeric materials, and a recycle system for passing unreacted materials past a cooler and compressor back to the top of the autoclave together with fresh monomer for replacing consumed monomer. At the downstream end of the autoclave, still active catalyst can be deactivated before a separation and compression stage by addition of suitable killer materials such as water. All the tests were at 1300 bar.
Where alumoxanes as scavengers were used, some hydrolysis of the scavenger material was performed on occasion to reduce the concentration of residual aluminium alkyl and to increase the average molecular weight of the alumoxane which was used as a starting material. The amount of such post-hydrolysis is indicated in the column "H_2O/Al mole ratio".

Example 1 (Comparative)

The process was performed in apparatus described in Exxon WO 92/14766. Polypropylene glycol (PPG) having a molecular weight of 2200 and a Mw value determined by GPC of 1.3 was used as a killer generally at a killer/TM1 mol ratio of 0.75, i.e. less than 1, often below 0.5 sometimes at 0.15 to suppress undesired polymerisation activity in separators and recycle.

A polymerisation process was performed using dimethylsilyl (bis-tetrahydroindenyl) zirconium dimethyl, hereinafter referred to as TM1, and a bulky anion cocatalyst, a dimethyl aniline ammonium salt of tetrakis perfluorotetraphenyl boron, hereinafter referred to as CC1. Polymerisation was at 160 °C using ethylene and 1-

butene. The TM1 / CC1 mole ratio was 3 to 1 as set out in Table 1 A and no scavenger was added. The properties of the polymer produced are set out in Table 1 B.

Example 2

This was performed similar to Example 1 but a higher aluminoxane, a hydrolysis product of tri-isobutylaluminum, referred to as IBAO, was used as a poison scavenger at a Al/CC1 mole ratio of 3. The IBAO has an average cryoscopically determined mol wt of 1770, and contained 5 mol % of residual tri-isobutylaluminum (TIBA). The TIBA was added with the fresh comonomer at the inlet of the recycle loop in a dilute solution in toluene.

The conditions and polymer properties are set out in Table 1 A and B. The reactor bottom temperature stayed around 180 °C. IBAO is not prone to recycle and will be removed with the polymer in the high pressure separator whilst at the same time IBAO has no cocatalytic activity. All the conditions were the same for the addition of scavenger. The catalyst productivity is enhanced by a factor three by use of a small amount of scavenger. At the small quantities employed, MAO would not be effective as cocatalyst and IBAO itself is much less active as a cocatalyst. It is presumed therefore that the increased productivity results from a cleaner system i.e. fewer Lewis-base type poisons.

Example 3 (Comparative)

Dimethylsilyl(bis-indenyl) hafniumdimethyl referred to herein as TM 2 and CC1 were used as catalyst. At a feed gas temperature of 30°C and a reactor temperature of 245 °C the reaction was unstable, and the reaction temperature could not brought less than 210°C, all this accompanied by very low productivity.

Example 4

Example was as Example 3 but IBAO intoluene was added to the catalyst vessel whereafter the pre-reacted TM2 and CC1 reaction product was added. By adding IBAO the reaction temperature remained controllable down to a temperature of about 170°C; the catalyst productivity became measurable; and an 80°C exotherm could be reached in the reactor leading to high conversions of monomer in the autoclave. The use of IBAO also permitted use of lower TM2/CC1 ratio.

The higher bottom temperature indicates that the catalyst remains active longer, but also incidentally produces a higher melt index material. Other polymer properties are unchanged, suggesting that IBAO is not catalytically active.

This catalyst gave a very narrow compositional distribution as shown by the compositional distribution breadth index.

Example 5

This was as Example 4 but post-hydrolysed methylalumoxane was used as a scavenger. A good temperature control and similar catalyst productivities were obtained. However, compared with Example 4 a lower bottom reactor temperature resulted.

Example 6, 7 and 8

Two catalyst components were used: dimethylsilyl (tetramethylcyclopentadienyl)(tert-butylamide)titanium dimethyl (referred to herein as TM3) and CC1. They were first pre-reacted in toluene in the glove box, and then added to a dilute toluene batch containing methylalumoxane (MAO) as poison scavenger. The TM3/CC1 ratio was 1.8 and the Al/TM3 mole ratio was 25. The catalyst was hydrolysed slightly on-line at a H_2O/Al mole ratio of 0.32.

By using different amounts of catalyst, the top reactor temperature was varied.

The reaction could not be run without MAO. The low levels of MAO are not normally associated with catalytic activity. At a top reactor temperature of 160°C the cat flow rate immediately ceased to rise and stabilised to give a catalyst productivity of 55 k gr PE/gr of CC1. The catalyst concentration was then doubled. The catalyst consumption then was such as to give a productivity of 105 k gr PE/g CC1 at a TM3:CC1 mole ratio of 2.75. Without hydrogen, the molecular weight was around 40 MI and the wt% C4 incorporated was 22%. In presence of MAO, the metallocene does not appear easily

deactivated by H_2O. Aluminoxanes are good poison scavengers for the catalyst system.

TABLE 1A

PROCESS/PRODUCT DATA

Example	Cat/Cocat.	TM/CC mole ratio	Scavenger	Al/TM mole ratio	H2O/Al mole ratio	Top/bottom reaction temp. in °C	C4/C2 wt ratio	Catalyst productivity PE/gr CC
1	TM1/CC1*	3.0	none	N/A	N/A	160/170	0.47	27000
2	TM1/CC1	3.0	IBAO (5mol% TIBA)	7	0	160/183	0.47	80000
3	TM2/CC1*	3.0	none	N/A	N/A	245/256	0.47	<10000
4	TM2/CC1	1.5	IBAO (5mol% TIBA)	35	0	170/248	0.40	65000
5	TM2/CC1	2.0	MAO (17mol% TMA)	30	0.16	170/195	0.40	70000
6	TM3/CC1	1.8	MAO (14mol% TMA)	25	0.32	160/189	0.65	200000
7	TM3/CC1	1.8	MAO (14mol% TMA)	25	0.32	195/211	0.40	70000
8	TM3/CC1	1.8	MAO (14mol% TMA)	25	0.32	185/205	0.40	130000

* COMPARATIVE

Table 1 B

Example	MI	Viscosity cp@ 190°	wt% C4 NMR	density gr/cc	Mw GPC	MWD GPC	Mn NMR	mp °C	CDBI
1	91.7		14.1	0.9010	31175	2.10	20190	91	84.9
2	332.0		14.8		22958	2.04	11254	91.2	83.8
3		55	21.8		3716	1.71	1908	62	95.7
4	45.4		19.1	0.8891	40173	2.55	21456	68.5	92.9
5	4.9		20.2	0.8885	67303	2.84	37269	108.9/63.9	
6	3.6		31.5	0.8733	82461	2.67	31375	105.1	75.5
7	6.3		22.0	0.8875	65110	2.89	19378	109.9	
8	3.2		20.7	0.8893	76685	3.11	31664	110.5	62.9

Total Al content can be determined by titration. The titration methods for determining the concentration of total Al including unreacted aluminum alkyl can follow the methods described in E. Wänninen and A. Ringbom, "Complexometric titration of aluminum", Analytica Chemica Acta 12, 308 (1955); F. Nydal "The indirect Complexometric Tr=itration of Aluminum: A study of the Wänninen-Ringbom Method" Talanta, 4 141 (1960) D.F. Hagen, B.G. Biechler, W.D. Leslie, and D.E. Jordan "Controlled deactivation-hydrolysis and determination of aluminum in aluminum alkyl compounds", Analytica Chemica Acta, 41, 557 (1968).

the amount of unreacted aluminum alkyl can be determined by a separate test as set out for example in:

E. Bonitz, Chemische Berichte 88, 742 (1955); K. Ziegler et al. Liebigs Ann. Chem. 629, 20 (1969); and G.A. Razuvaev and A. Graevskii Doklady Akt. Nauk, SSSR 128, 309 (1959).

These methods can be adapted for the selective titration of free unreacted aluminum alkyl that is to say aluminum alkyls which will dissociate from the alumoxane in ~~an~~ appropriate solvent. The percentage unreacted aluminum alkyl on the basis of the total Al content can then be calculated.

Using the invention it is possible to obtain a catalyst productivity of over 200 000 gr PE/gr anion at a 1.8 TM activator mole ratio in the presence of an over-hydrolysed MAO (Al/TM = 25). The effect was especially pronounced with monocyclopentadienyl derivatives.

Using the invention a temperature split profile of 75 °C (170-245 °C) across a reactor was obtainable using presence of IBAO (hydrolysed isobutyl aluminum),

indicating that the catalyst remains very active at elevated temperatures while making a polymer of high molecular weight .

The features mentioned in the following claims may be combined with one another as may appear appropriate regardless of the appendancy.

CLAIMS

1. Use of a partially hydrolysed aluminum alkyl material oligomer as a scavenger in an olefin polymerisation process, said material containing less than 20 % by Al on the basis of the total Al content of unreacted aluminum alkyl, preferably less than 15 %, especially less than 10 %.

2. Use according to claim 1 wherein the oligomer is derived from an aluminum alkyl containing an alkyl group with at least two carbon atoms and has substantially no co-catalytic activity, preferably being derived from an alkyl group containing a tertiary carbon atom.

3. Use according to any of the preceding claims 1 or 2 in which the material is used as a scavenger by adding to a catalyst system prior to the introduction of the catalyst system to a polymerisation reactor and/or separately to a polymerisation reactor feed before or after the introduction of the feed to the reactor.

4. A continuous process for olefin polymerisation including injecting as catalyst a bulky ancillary ligand transition metal component and a bulky anion precursor or a reaction product thereof into a reactor, feeding monomer to the reactor and withdrawing polymer therefrom in which there is additionally added as a scavenger an oligomer of a partially hydrolysed aluminum alkyl oligomer containing less than 20 % by Al of unreacted aluminum alkyl, preferably less than 10 %

5. A process according to claim 4 which the scavenger is added to the catalyst before introduction into the reactor and/or to the monomer fed and/or polymerisation reactor.

6. Process according to claim 4 or claim 5 in which the mol ratio of the transition metal component and the cocatalyst is from 1:10 to 10:1, preferably from 1:1 to 3:1 and/or in which the mol ratio of aluminum in the scavenger to the transition metal in the transition metal component is from 1:1 to 500:1 preferably from 2:1 to 50:1.

7. Processs according to any of the preceding claims in which the oligomer is derived from an aluminum alkyl having alkyl groups with from 2 to 20 carbon atoms and it includes preferably at least one tertiary carbon atom.

8. Process according to any of the preceding claims 4 to 7 in which the partially hydrolysed aluminum alkyl has a molecular weight of at least 800, preferably 1000.

9. Process according to any of the preceding claims 4 to 7 in which the catalyst is unsupported and preferably the polymer and monomer are in a homogeneous medium and/or in which the reaction temperature is from 100 to 300°C preferably from 150 to 280°C and/or in at a pressure of from 100 to 3000 bar.

10. Process according to claim 9 in which a mixture is withdrawn from the reactor, polymer is separated and a residue containing unreacted monomer is recycled to the reactor.

11. Continuous process for olefin polymerisation including injecting as catalyst a bulky ancillary ligand transition metal component and a bulky anion precursor or a reaction product thereof into a reactor, feeding monomer to the reactor, polymerising-monomer at from 100 to 300°C at up to 3000 bar in the reactor and withdrawing polymer from reactor in which there is additionally added as a scavenger an oligomer of a partially hydrolysed aluminum alkyl oligomer.

12. Process according to claim 11 in which the oligomer is derived from an aluminum alkyl containing at least two carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/03119

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/602

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 14132 (THE DOW CHEMICAL COMPANY) 22 July 1993 cited in the application see page 4, line 6 - line 14; claim 1 ---	1-12
X	EP,A,0 513 380 (IDEMITSU KOSAN CO. LTD.) 19 November 1992 cited in the application see claim 2 -----	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
10 February 1995	24. 02. 95

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INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No
PCT/EP 94/03119

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9314132	22-07-93	EP-A- 0574561 JP-T- 6505767	22-12-93 30-06-94
EP-A-0513380	19-11-92	WO-A- 9209640 JP-A- 5202125 US-A- 5369196 JP-A- 5043618	11-06-92 10-08-93 29-11-94 23-02-93